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U.S. Army Research, Development and Engineering Command

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

BLACK SILICON FOR NEXT-GENERATION INFRARED SENSORS

Dr. Jeffrey Warrender

August 2012

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Sionyx, Inc.	Martin Pralle, Jim Carey

DoD applications require Infrared light

Precision-guided munitions

Situational Awareness

Hyperspectral weapon sights

Photovoltaics

Standoff Explosive Detection

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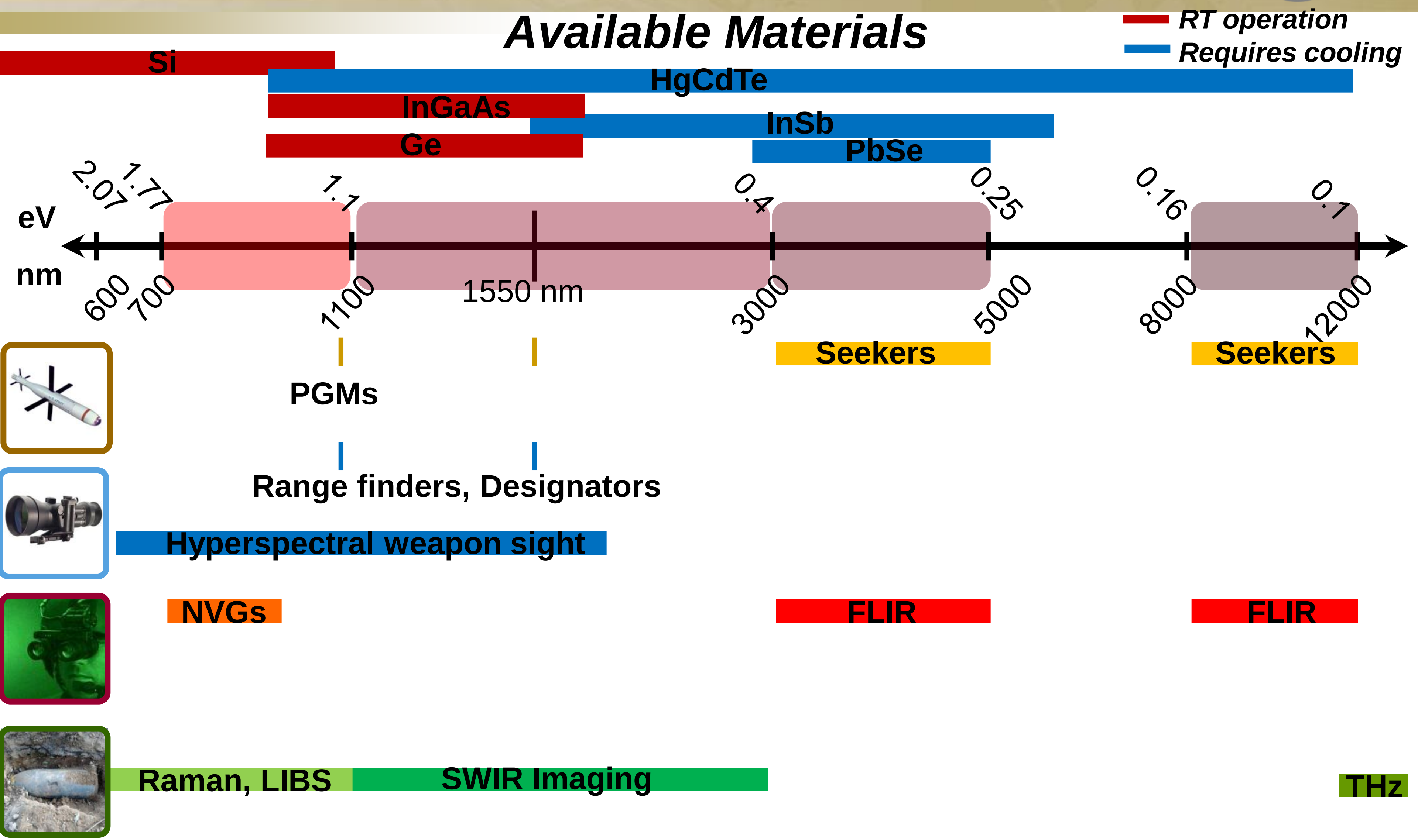
Available Materials



Malcolm Baldrige National Quality Award 2007 Award Recipient

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

Silicon-based IR optoelectronics

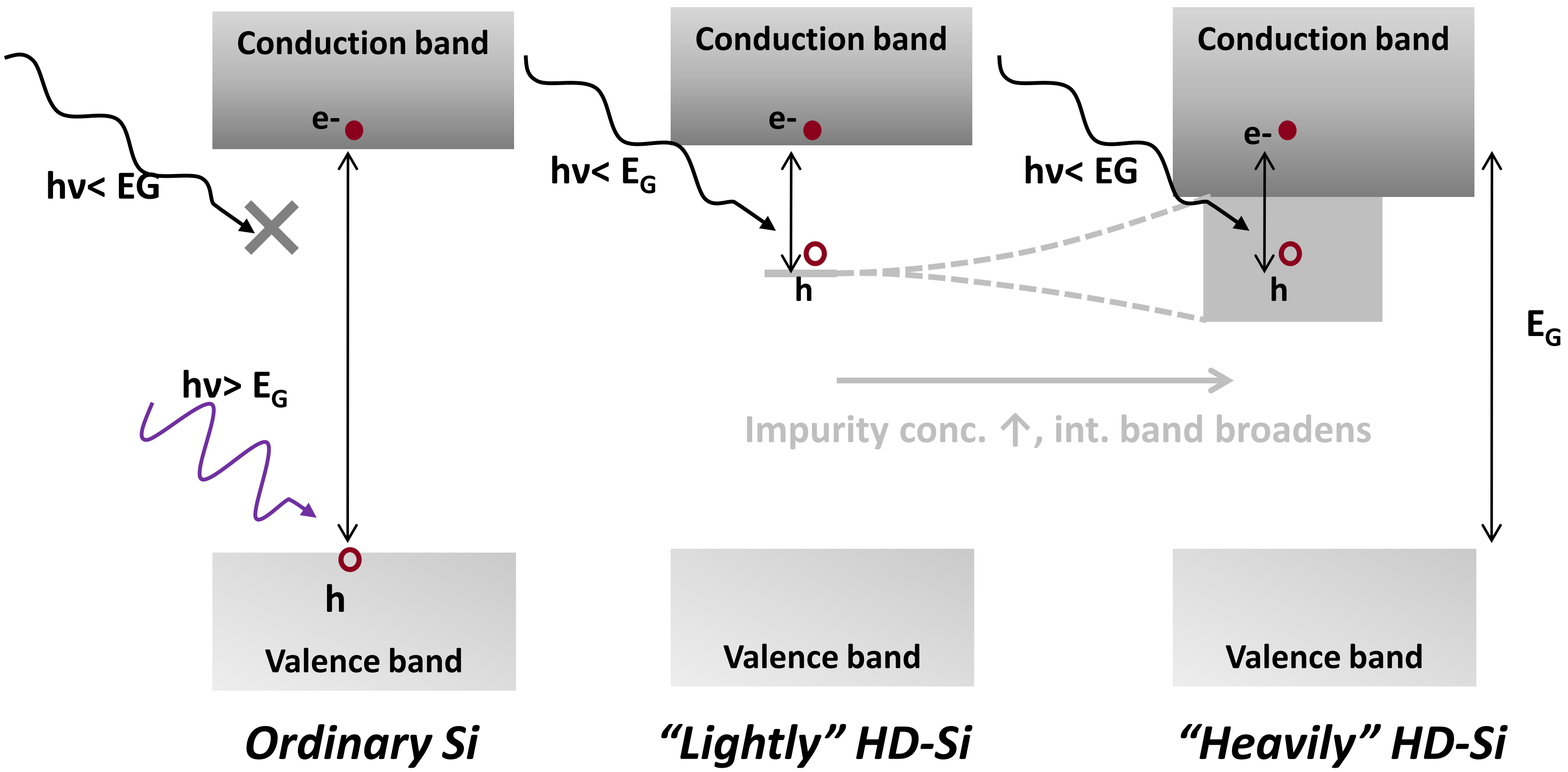
Silicon is…

+
- **Ubiquitous**
- **Inexpensive**
- **Well-characterized**
- **Easy to integrate with readout circuitry**

-
- **Non-absorbing for wavelengths > 1100 nm**

Can we dope Si to see IR response?

Hyperdoping: Create mid gap states



Chalcogen dopants in silicon

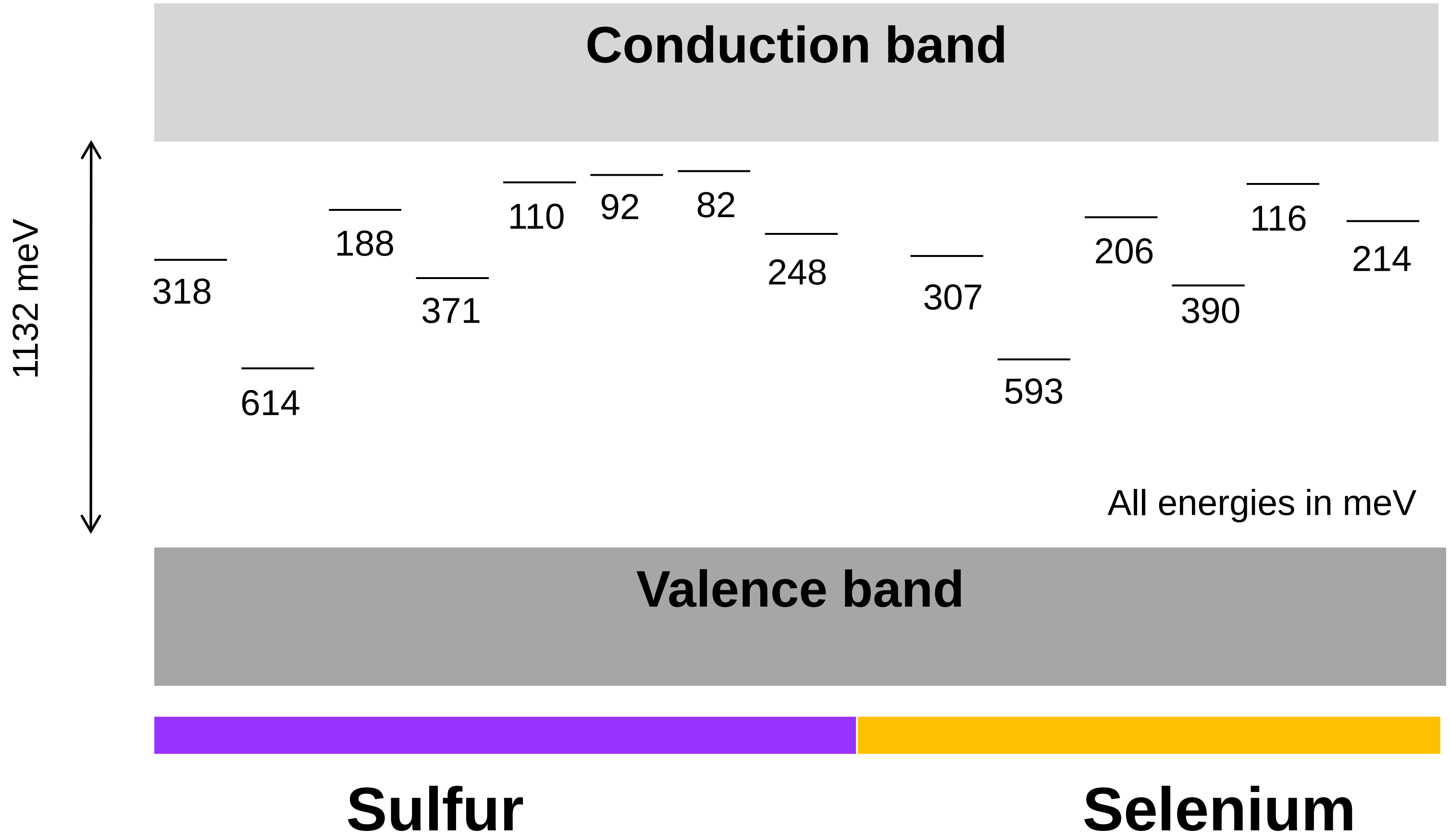
The Periodic Table of the Elements

1 **H** Hydrogen 1.00794																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012182											5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.00674	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.9984032	10 **Ne** Neon 20.1797
11 **Na** Sodium 22.989770	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.981538	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973761	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.955910	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.938049	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933200	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.96	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.90585	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90638	42 **Mo** Molybdenum 95.94	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.90545	56 **Ba** Barium 137.327	57 **La** Lanthanum 138.9055	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.078	79 **Au** Gold 196.96655	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98038	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (262)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92534	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93032	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93421	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
90 **Th** Thorium 232.0381	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.0289	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

Chalcogen dopants in silicon

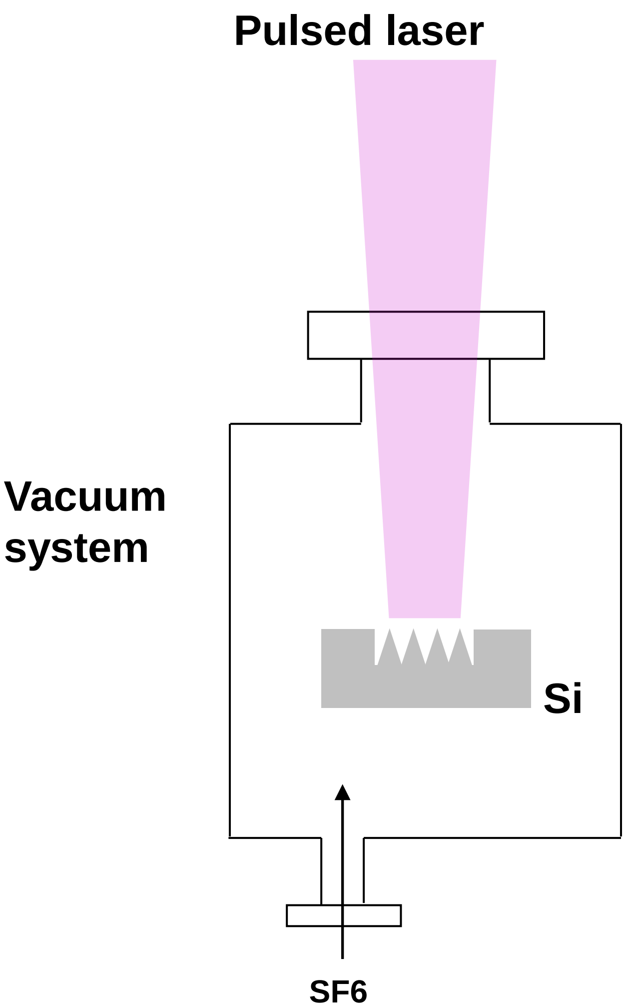
Binding energies of chalcogen centers in Si



Janzen et al., *Phys Rev B* (1984)

Spiked Black Silicon

Harvard (Mazur)/ Sionyx



Crouch *et al*, *Appl Phys Lett* (2004)

Spiked Black Silicon

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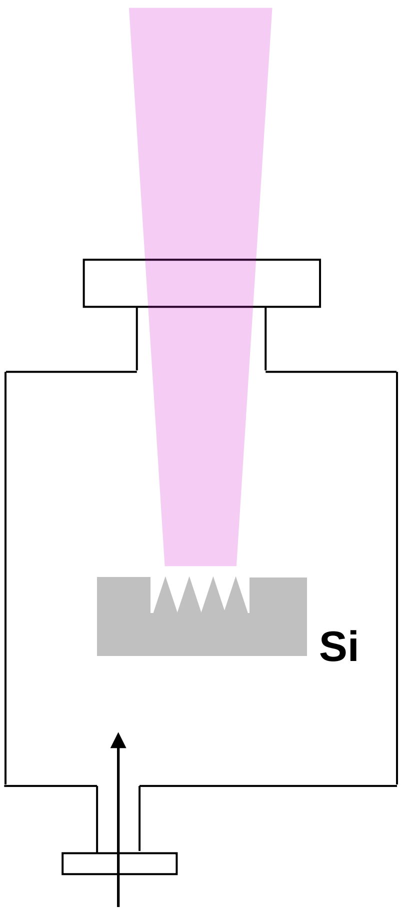
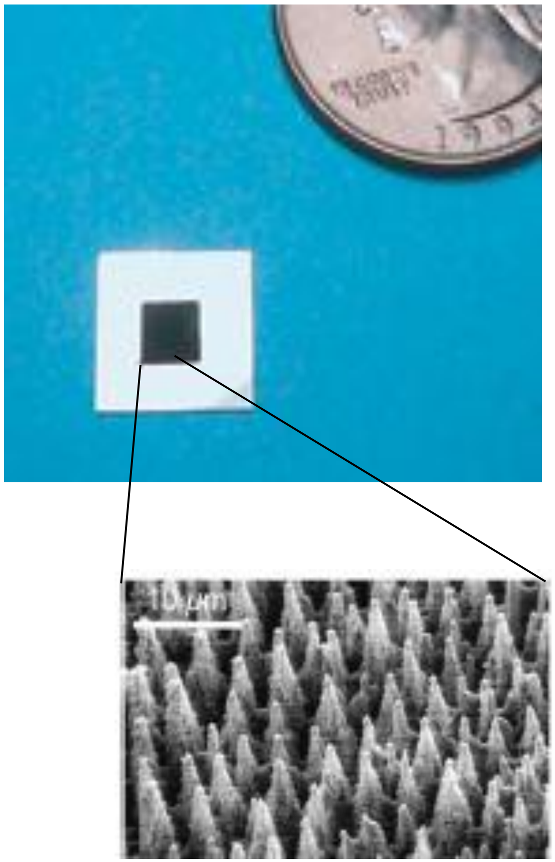


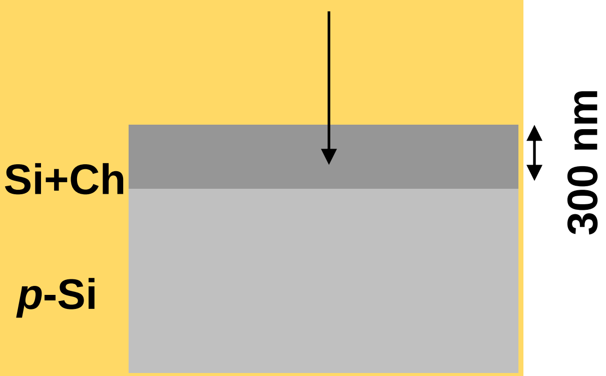


Crouch *et al*, *Appl Phys Lett* (2004)

Flat Black Silicon

Harvard (Aziz)/ ARDEC

(1) **Ion-implant chalcogen (S, Se, Te) into p-Si**



Kim *et al*, *Appl Phys Lett* (2006)
Tabbal *et al*, *JVST B* (2007)

Bob *et al*, submitted to *J Appl Phys*

Flat Black Silicon

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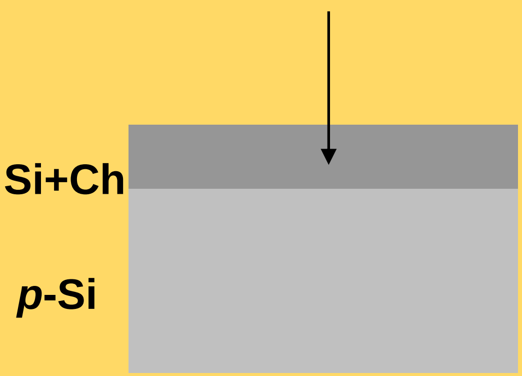
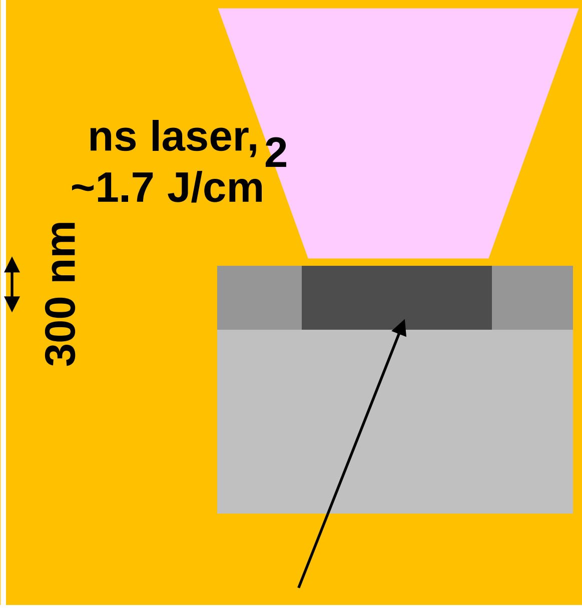
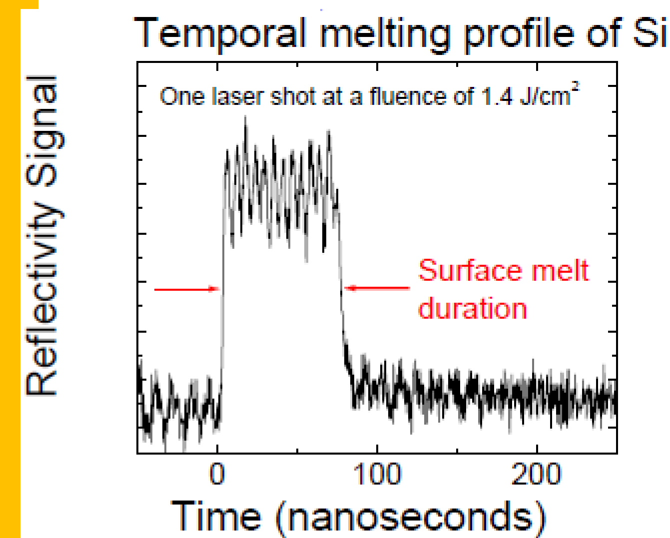


(2) **Pulsed-laser melting (PLM) "heals" implant damage**



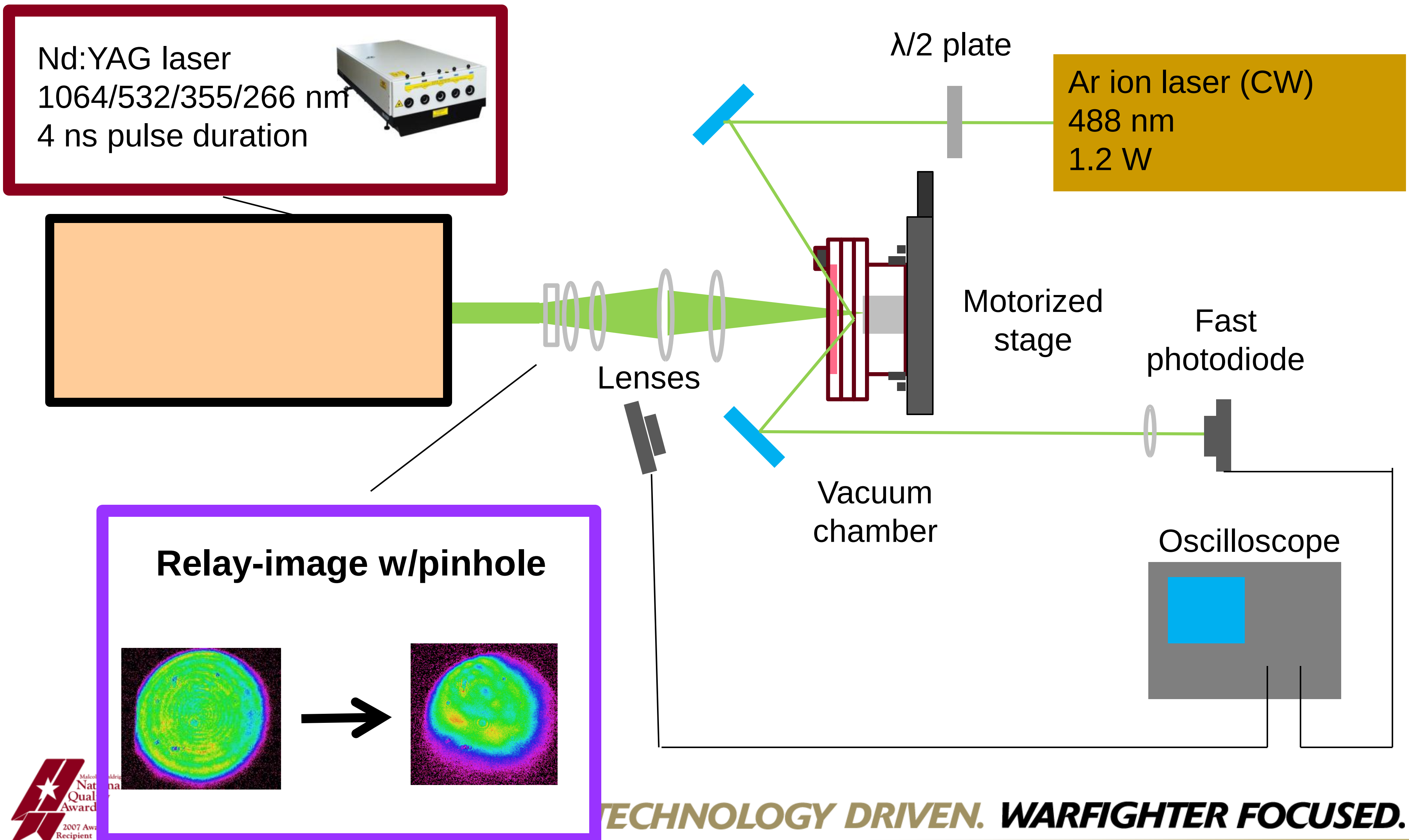
Crystalline Si, supersaturated in Ch, *n*-type



Kim *et al*, *Appl Phys Lett* (2006)
Tabbal *et al*, *JVST B* (2007)

Bob *et al*, *JAP* (2010)

Benet Labs' Black Silicon setup



Characterization Logical Flow

Structure

• Dopant profile
• Surface roughness
• Crystallinity
• Local dopant environment

Absorption

• Absorption vs. wavelength
• Depth profile
• Modeling

Electronic properties

• Carrier sign, concentration, mobility, lifetime
• Hall effect

Optoelectronic Properties

• Photoconductivity
• Spectral responsivity
• Quantum Efficiency
• IV curves
• Gain

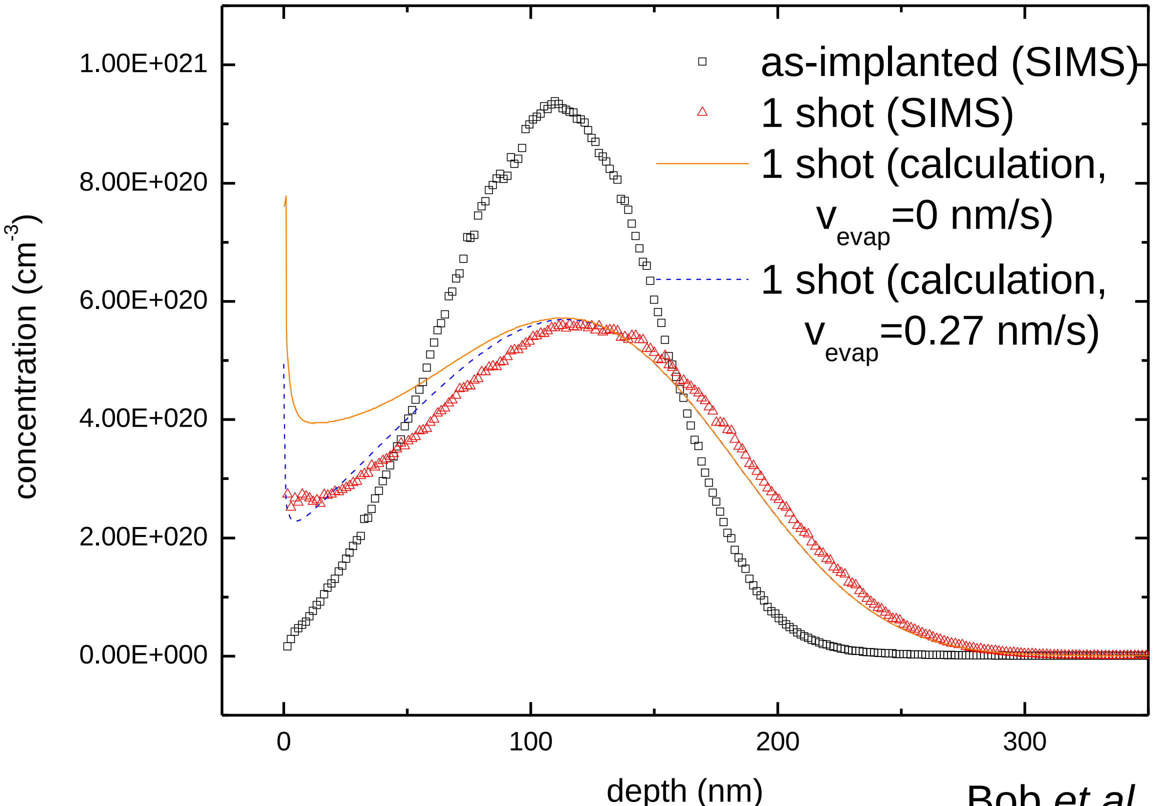
Device Properties

• Detectivity
• Noise Equivalent Power
• Dark current

6.1 → 6.2

Structure

Dopant depth profile evolution



Bob *et al*, *JAP* (2010)

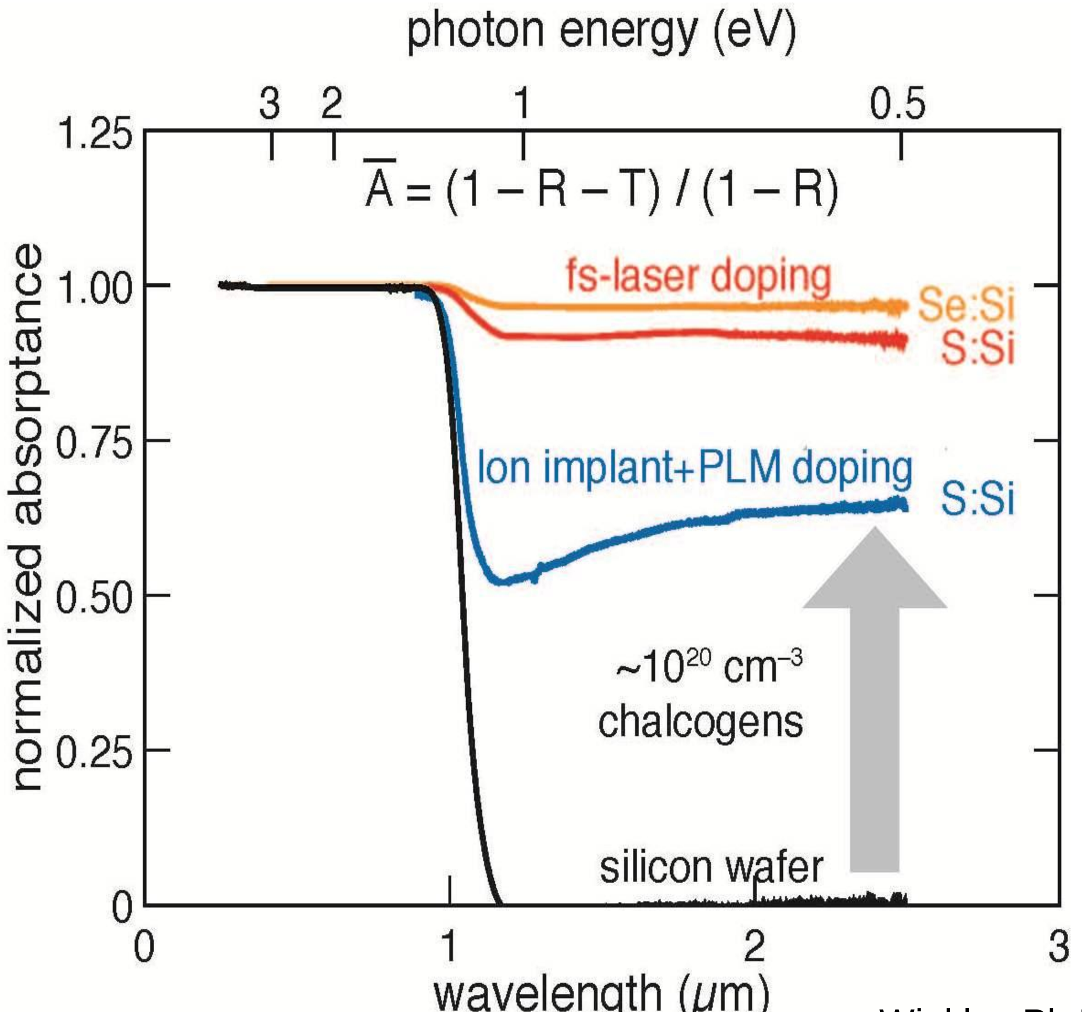
BUT, as laser shots ↑, v_{evap}↓

Our approach to studying hyperdoped silicon

Path to detection	A photon is absorbed	A mobile carrier is generated	The carrier reaches a contact	The carrier is collected
Obstacles to detection		No free carriers are generated	No carriers reach the contacts	No carriers are collected
Major questions	How does absorption occur?	Is the excitation mobile?	How far can the excitation travel?	
Experimental approaches	Direct optical probes	Photoexcitation measurements	Transport measurements	

Absorption

Absorption

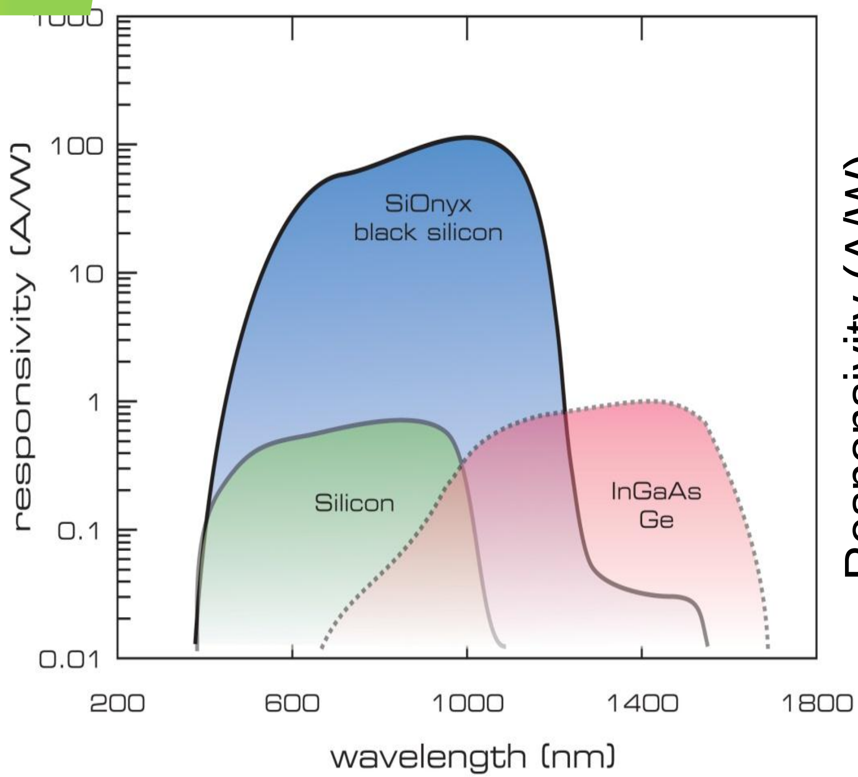


Winkler, Ph.D. thesis, Harvard (2010)

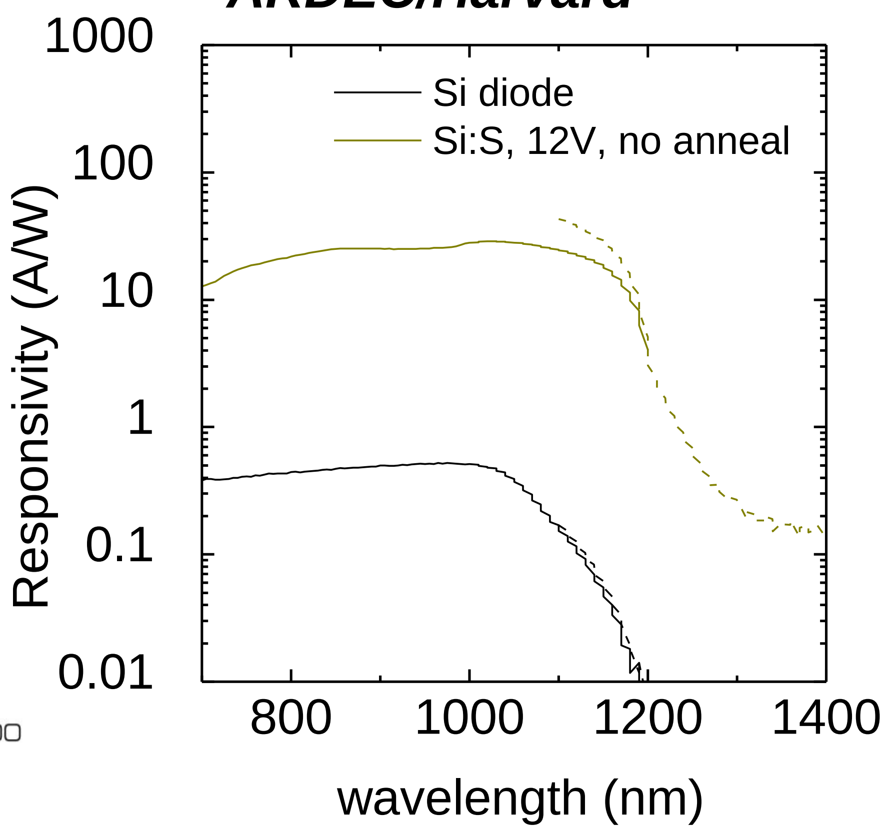
Responsivity comparison

Optoelectronic Properties

Sionyx

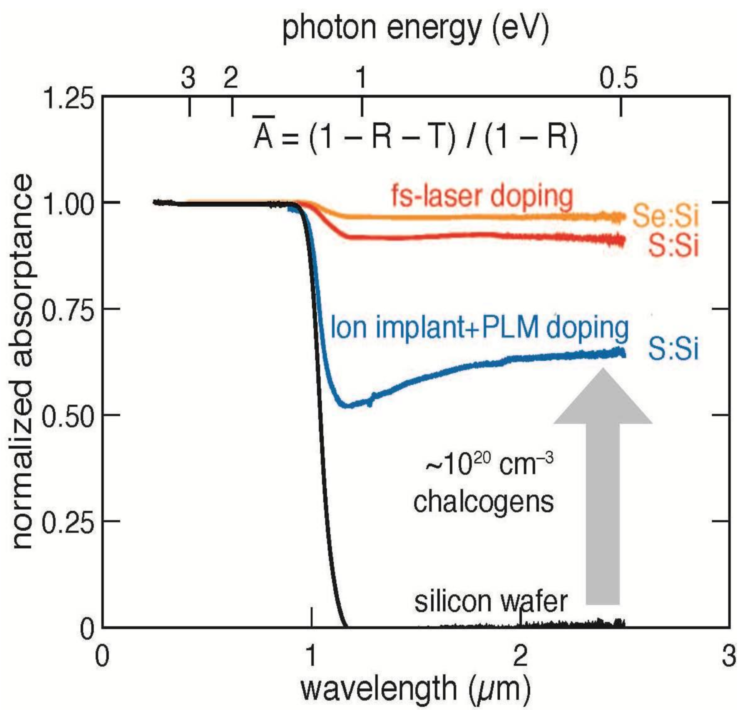


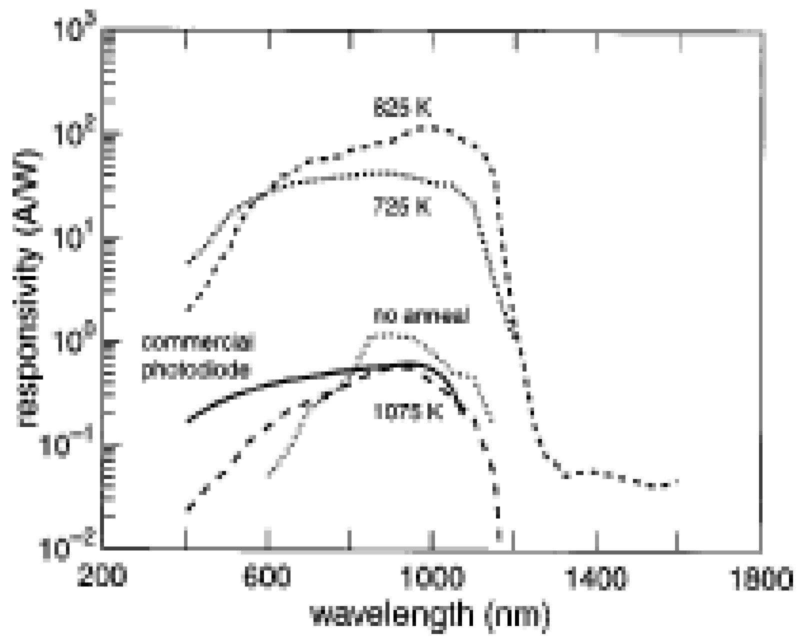
ARDEC/Harvard



Said et al, *APL* (2011)

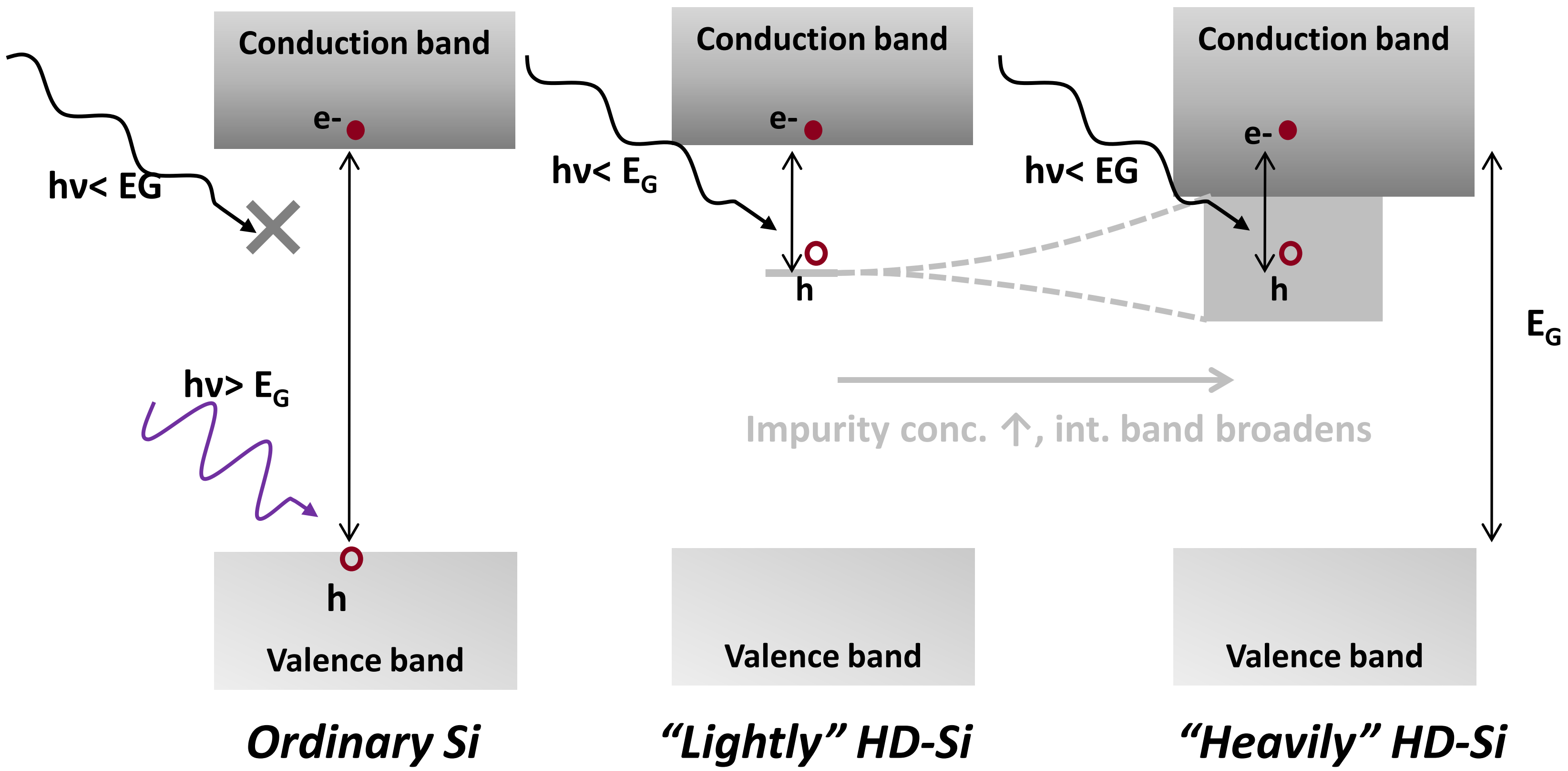
An apparent conundrum



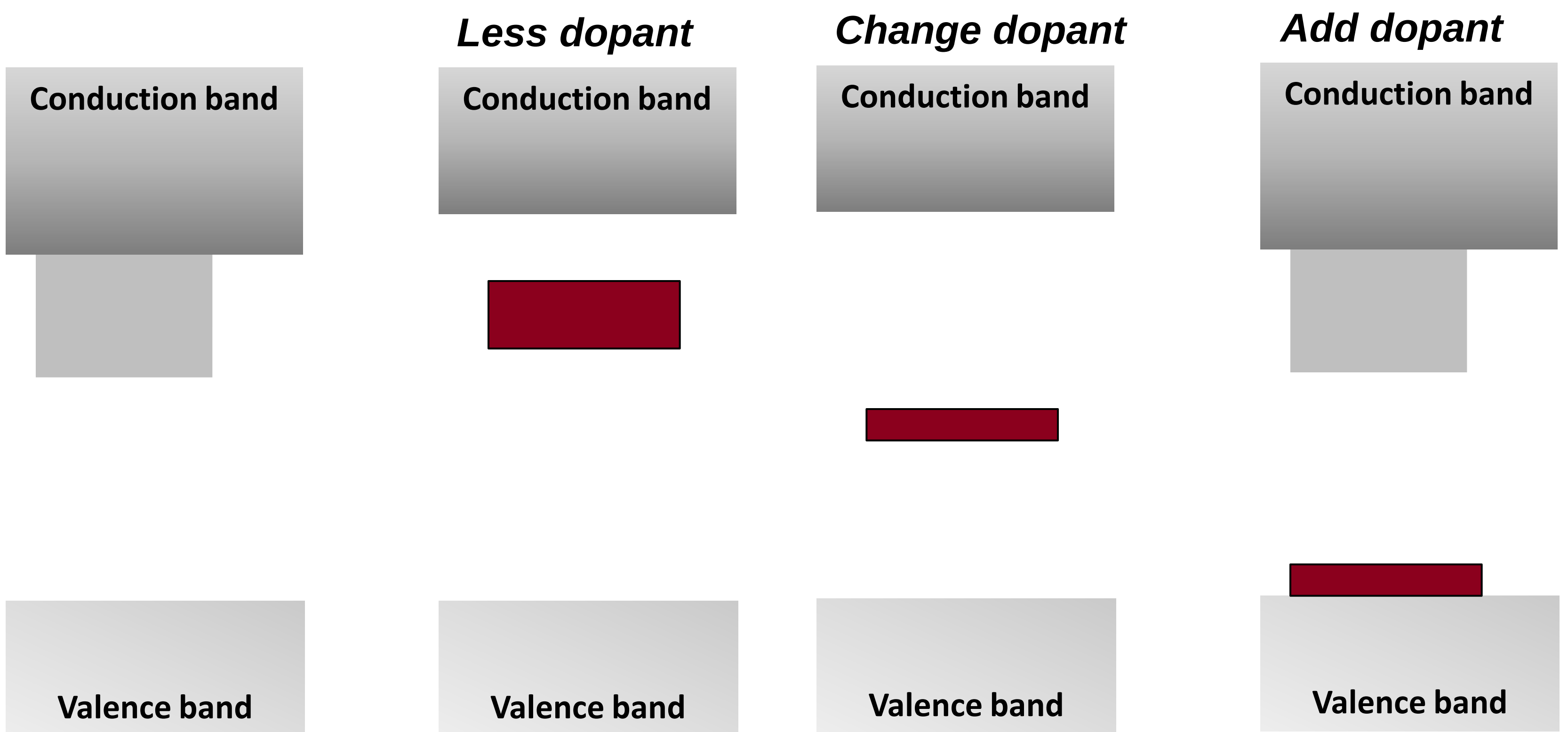


Strong, broadband absorption… **…but no device response**

Possible reconciliation



Other Strategies to Try



Move states out of conduction band

Move states deeper into band gap

Compensate impurity band

The Larger Black Silicon Universe

Stakeholders

	System	Existing BSi ok?	Extended IR needed?
CERDEC-NVESD	Digital Nightvision	X	
USMC	CLRF	X	X
ONR	DETECT, CLRF	X	X
White Sands Missile Range	Airborne Laser	X	
ARDEC	Precision-guided	X	X

Research Groups

Extended IR response, optoelectronic charazterization:
- **Harvard** *Aziz*
- **ARDEC-Benet** *Warrender*
- **RPI** *Persans*
- **MIT** *Buonassisi*

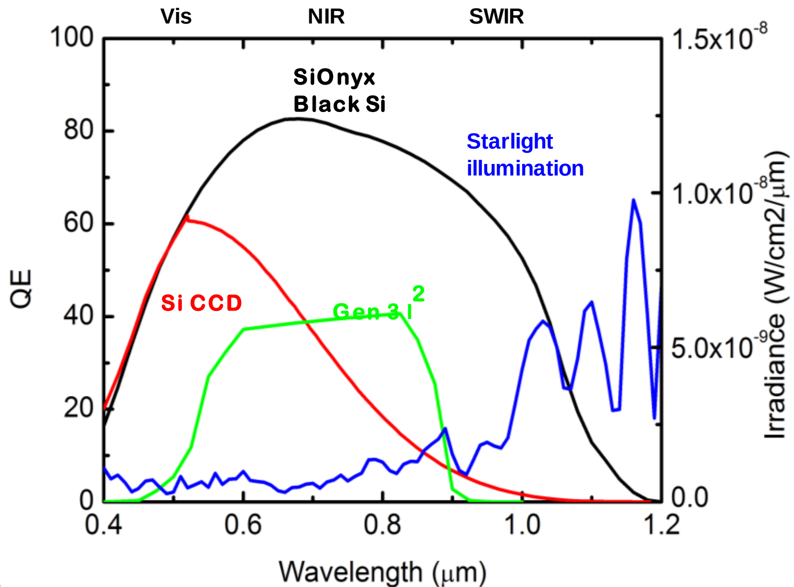
Characterization of fs-structured Black Silicon:
- **Harvard** *Mazur*
- **MIT** *Gradecak*

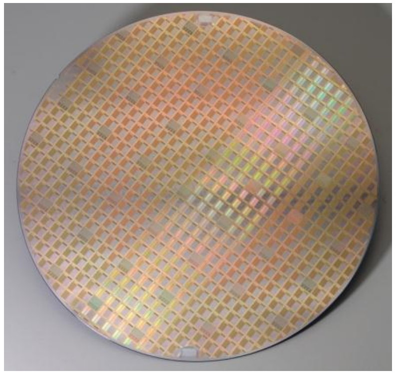
First principles modeling:
- **MIT** *Grossman*
- **Illinois** *Ertekin*

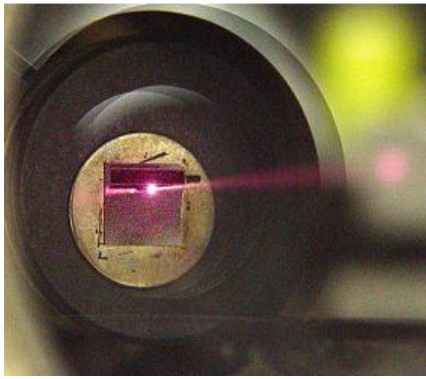
Commercialization:
- **Sionyx** *Pralle, Carey*

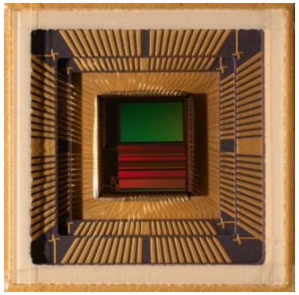
SiOnyx IR CMOS: Black Silicon enhanced imaging

Imaging from UV to NIR/SWIR









- Low cost 8" CMOS manufacturing
- Low Noise (Read noise ~2 e/pix) (Dark Current <8e/pix/frame)
- Low Power (300 mW @ 800x600)
- Compact Size
- TRL 6 imaging device
- TRL 6 wafer process

mupralle@sionyx.com, 978-922-0684x127

Outreach

Black Silicon Quarterly

- News and recent black silicon goings-on
- Send an email to jeffrey.m.warrender.civ@mail.mil to be added to distribution

Issue 01 January 2012

Black Silicon Quarterly

CHRONICLING PROGRESS IN LASER HYPERDOPED MATERIALS RESEARCH

ABOUT BLACK SILICON

"Black" Silicon is the name given to laser hyperdoped silicon, which was discovered in 1999 by Prof. Eric Mazur at Harvard University.

The name "black silicon" invokes the modification to the optical properties of ordinary silicon, which can result either from structuring of the surface, or introduction of an excess of a dopant, or from both.

Because of its strong visible and infrared absorption, and high device response, this material has applicability to sensing and imaging in the visible, near infrared, and short-wave infrared, as well as to photovoltaics. Because it is silicon-based, devices made from black silicon should be comparably inexpensive.

This Issue

Welcome to *Black Silicon Quarterly*

Black Silicon Quarterly is a new newsletter that will be released approximately quarterly by the U.S. Army's ARDEC-Benet Laboratories, to disseminate recent research findings and news items of interest from the worldwide community engaged in research on laser hyperdoped silicon and related materials.

Black silicon holds great promise for inexpensive photodetection and imaging in the visible, near-infrared, and short-wave infrared regions of the electromagnetic spectrum. Because of the numerous applications that could benefit from a low-cost, silicon-based solution to sensing and imaging, black silicon has numerous stakeholders within the U.S. Department of Defense, Department of Energy, Department of Homeland Security, and industry.

From its early days in a single group at Harvard University, the black silicon research field has grown to a burgeoning community of researchers at top American universities such as Harvard, MIT, Rensselaer, and University of Illinois Urbana-Champaign, international universities, government labs, and one start-up company, Sionyx, Inc.

Black Silicon Quarterly seeks to act as a conduit between the stakeholder community and the research and development community. It will collect and condense recent activity in the research community, so that stakeholders can stay abreast of the latest data on this emerging technology.

Black Silicon Quarterly welcomes submission of relevant news items, publication announcements, upcoming meetings and symposia, or other items of interest to the research and stakeholder communities.

Black Silicon Symposium

- Held in Albany, NY
- **August 9-10**

Summary and Outlook

- **Laser hyperdoped "black" silicon can be made by two different approaches**
  - Similar properties
  - "Flat" black silicon easier to study

- **Strong sub band gap absorption**
- **High EQE out to 1200 nm**

- **ARDEC seeks to extend strong device response to 1700 nm**

- **Fundamental and practical questions abound**

jeffrey.m.warrender.civ@mail.mil

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BACKUP SLIDES

Malcolm Baldrige National Quality Award 2007 Award Recipient

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Research interests at Benet

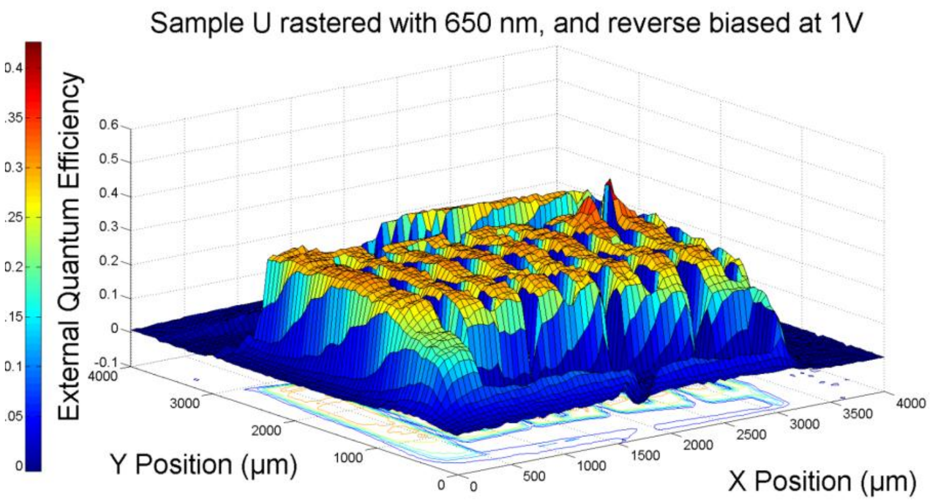
- Extending black silicon's IR response
- Characterizing the properties of ns-spiked black Si
- Exploring broader slice of parameter space
  - Non-chalcogen dopants, thick layers, 5 ns pulses, non-UV wavelengths
- Increasing process cleanliness
- Black Si photovoltaics

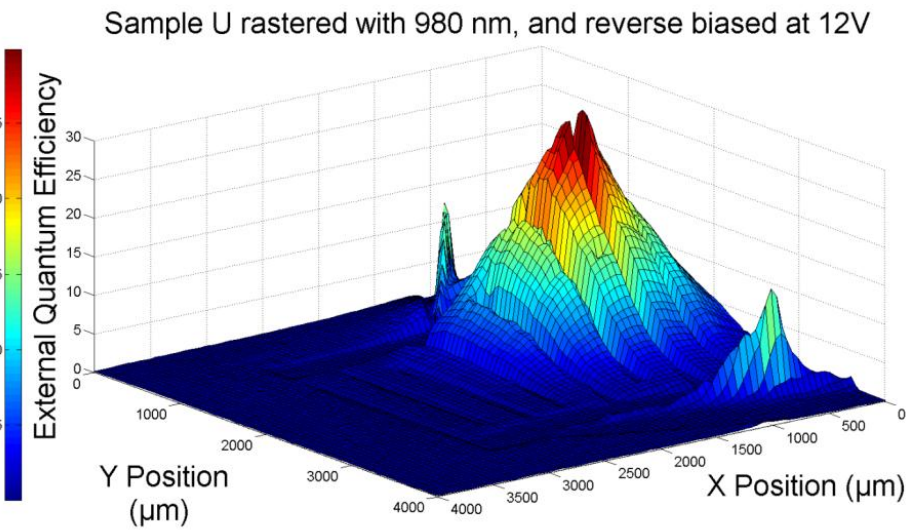
Assets

Laser/tool	Purpose	Capabilities
Ekspla NL313	Laser melting	532 nm/ 355 nm 800/500 mJ output 5 ns pulse duration
Coherent I-306	Surface reflectivity	514/488/458 nm 2.4/1.8/0.42 W output CW
Resonetics Excimer system	Laser melting	248 nm 400 mJ output 20 ns pulse duration
Vacuum chamber with motorized stage	Wafer-scale clean processing	150 mm Si wafer processing
Dual-beam FE-SEM/FIB	TEM sample prep, High-res imaging	System spec pending

Optoelectronic Properties

Gain is spatially inhomogeneous





Optoelectronic Properties

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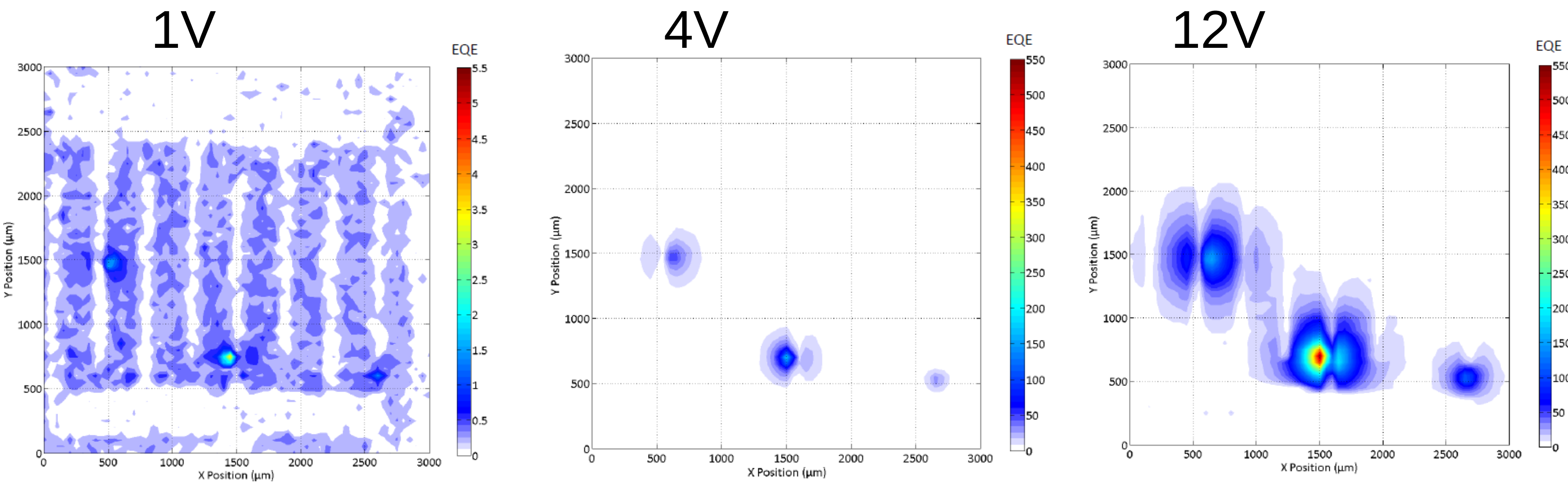
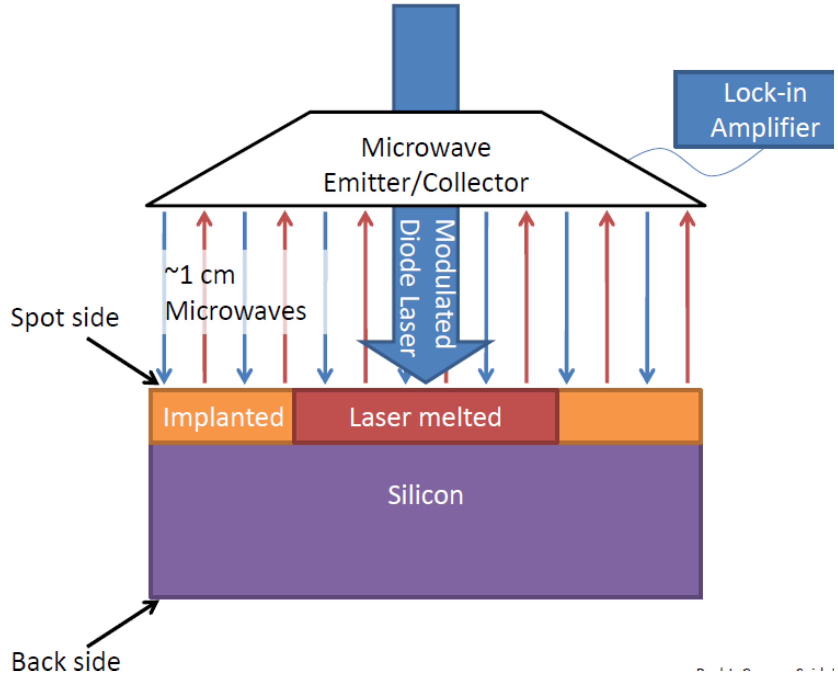
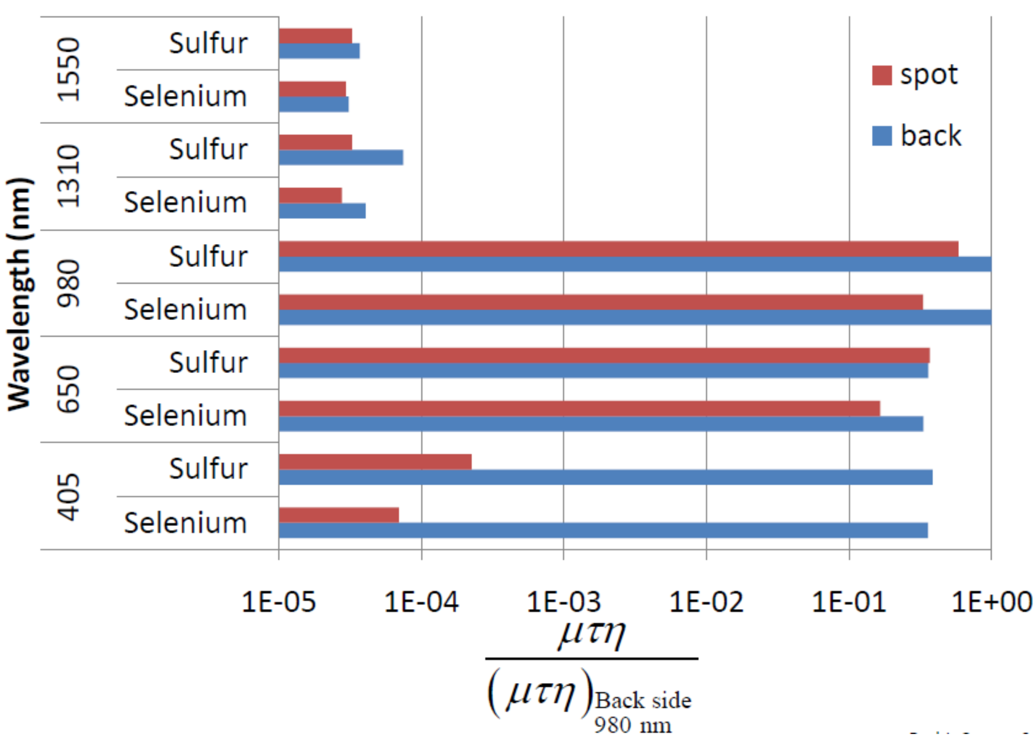


1e15/cm^2 S in Si, 4 laser shots, Ti/Ni/Ag contacts, 980 nm probe laser, reverse bias

…but the story gets even weirder

Microwave reflectivity

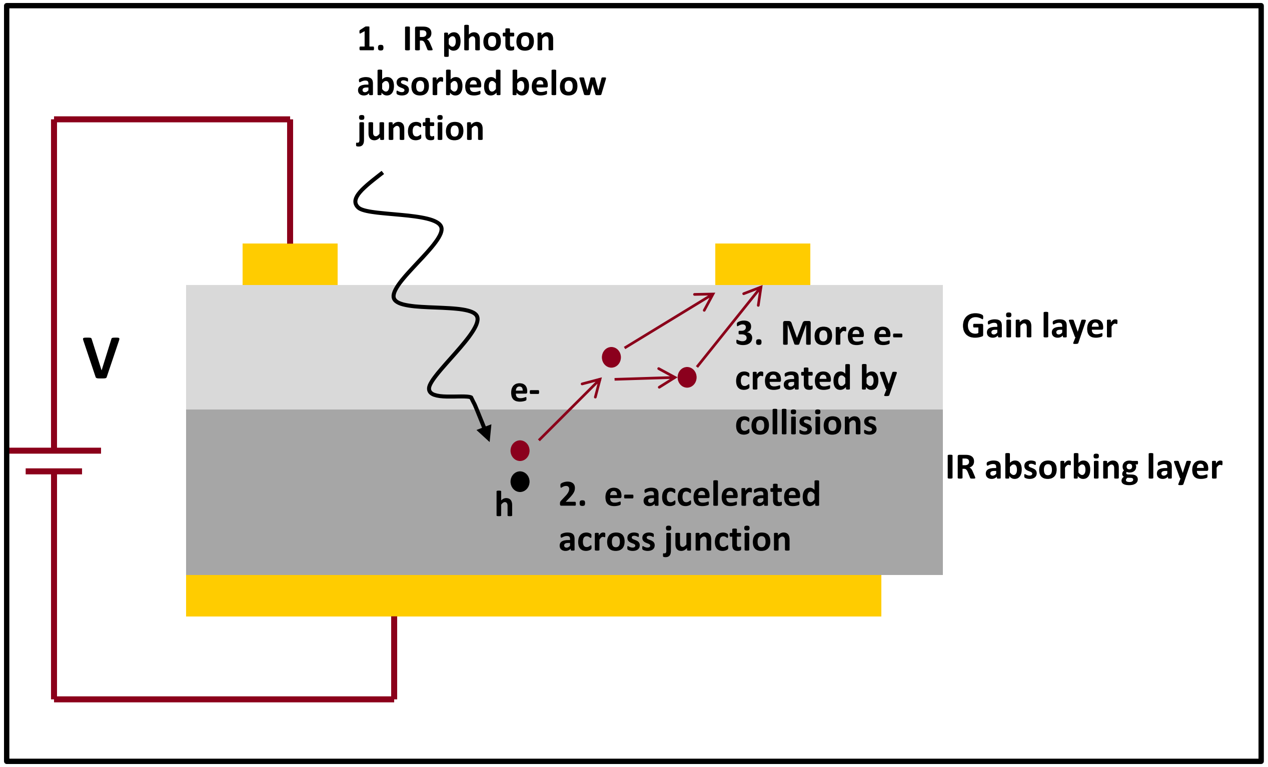




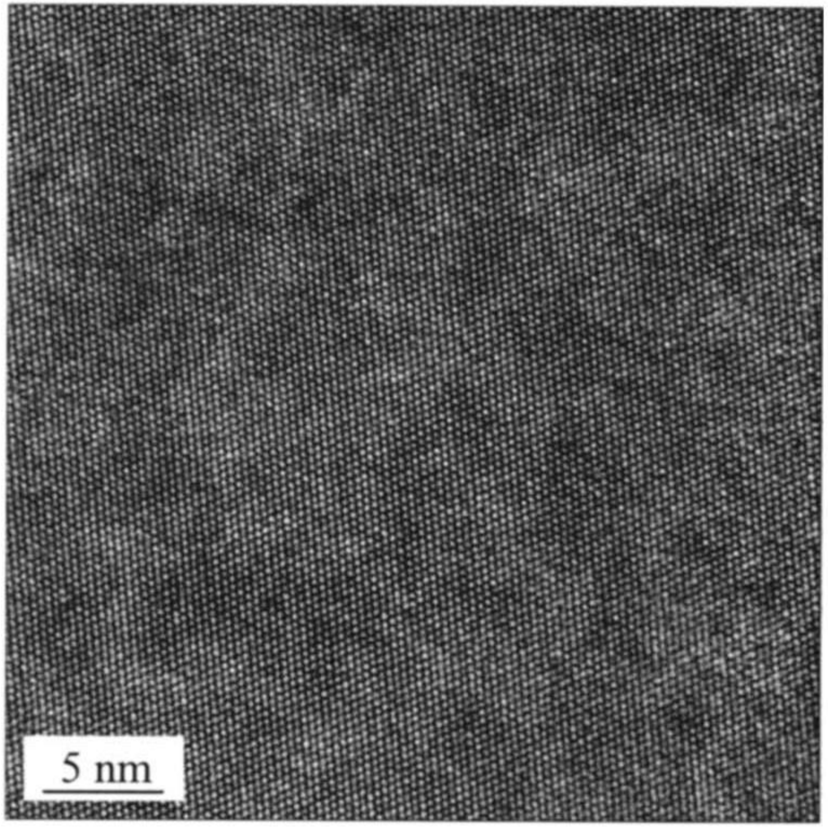
No detectable photoconductivity in the Si:S layer!

Optoelectronic Properties

Gain without photoconductivity?



XTEM lattice image of PLM'd material



Data were converted to signal per (pump photons per second)

$$\text{photoinduced microwave reflectivity} \times \frac{\text{pump energy per photon}}{\text{Pump power} \times \text{1-Reflectance}} = \text{Signal/(pump photons per second)}$$

$$\frac{C\Delta\sigma}{\text{photons / sec}} = \frac{Ce\mu\Delta n}{\text{photons / sec}} = \frac{Ce\mu\tau g}{\text{photons / sec}} = \frac{(Ce\mu\tau)\times(\text{photons / sec})\times(\eta)}{\text{photons / sec}} = Ce\mu\tau\eta$$

Constant dependent on apparatus not sample or pump

Taking the ratio of two measurements removes the influence of the experimental apparatus (*C* cancels out)